

# Aerospace Research Center

MATERIALS DEPARTMENT

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HIGH TEMPERATURE STABLE CARBORANE ADHESIVES

CONTRACT NASA 9-5527

Third Quarterly Progress Report

by

Dr. Robert Barnes

Submitted to:

National Aeronautics and Space Administration  
Manned Spacecraft Center  
2101 Webster-Seabrook Road,  
Houston, Texas.

October 15, 1966

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Approved:



Dr. Daniel Grafstein,  
Principal Staff Scientist  
Manager, Materials Department

October 15, 1966

## ABSTRACT

Contract NASA 9-5527

This is the third quarterly report on the synthesis and evaluation of carborane-epoxy adhesives for high-temperature aerospace applications. This report covers technical progress for the period from June 21, 1966 to September 20, 1966.

During this period, progress was noted as follows:

1. Adhesive Bond Property Evaluation (Phase IV)

The use of epoxyalkylcarborane systems as adhesives has now been demonstrated. Lap-shear specimens were assembled using catalyzed mono- and bis(epoxybutyl)carborane as the adhesives. Room temperature bond strengths of up to 1560 p.s.i. were obtained in the initial samples where both adhesive and cohesive failure were observed.

2. Curing and Polymerization Studies (Phase III)

Studies were conducted on the polymerization of mono(epoxybutyl)carborane and bis-(epoxybutyl)carborane using: DMP-30, N,N-dimethylbenzylamine and Boron trifluoride-monoethylamine as catalysts.

The most promising systems observed to date were generated with the boron trifluoride-monoethylamine catalyst. At 150°C, bis(epoxybutyl)carborane sets almost immediately to a non-flowing viscous liquid. After one hour, the sample was a hard solid at 150°C which, at room temperature, was not easily fractured.

3. Synthesis of Carborane-epoxy Monomers (Phase II)

Mono(epoxybutyl)carborane was prepared again by the following reaction route.

## ADMINISTRATIVE INFORMATION

This 12-month program is being sponsored by the NASA-Manned Spacecraft Center, Houston, Texas under Contract NASA 9-5527, Control No. P.R. No. 5320022.

This Quarterly Report covers the period from June 21, 1966 through September 20, 1966.

The NASA Technical Representative is Mr. Ivan K. Spiker/ES4. The Project Supervisor at the General Precision Aerospace Research Center, 1225 McBride Avenue, Little Falls, New Jersey is Dr. Daniel Grafstein. The principal contributing personnel are Dr. Robert Barnes and Dr. Edward Hughes. Infrared spectra were obtained with the assistance of Mr. Lawrence Flint and Mr. Clifford Whitmore.

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## I. INTRODUCTION

The object of this program is the synthesis of adhesives that are stable above 600°F, and as high as 1000°F for aerospace applications. To achieve this objective, we are preparing epoxy adhesives containing carborane units in the monomer structure.

Aside from the problem of thermal stability, conventional epoxies offer an unlimited scope of modification and application possibilities. However, the best epoxy systems, such as those derived from bis-phenol A, are not serviceable above 350°F. Combined epoxy phenols are very versatile adhesives and are serviceable to 350°F continuously. They retain satisfactory strength for short exposures up to 500°F. One solution to this dilemma is to try to incorporate a group into the system which serves to increase thermal stability without detracting from the favorable properties of the epoxy. Since the carborane polyhedron appears to impart excellent thermal and physical properties to polymer structures, it seems natural to construct a polymer system which combines a carborane moiety with an epoxy function.

Several research groups have concentrated recently on the synthesis of high-temperature-stable polymers by the incorporation of carborane and neocarborane units into polymer structures with other groups<sup>(1)\*</sup>. The increased thermal stability of these polymers over conventional systems is due in part to the electron deficiency of the carborane group and its influence on the thermal stability of adjacent chemical bonds. The bulky, three-dimensional ring system also induces a degree of internal plasticization in the polymer, presumably because it prevents close-packing of the polymer chains.

During the first quarter<sup>(2)</sup>, efforts were directed toward the synthesis and accumulation of significant quantities of intermediates for the preparation of several epoxyalkylcarboranes and diepoxyalkylcarboranes. In particular, the effort was concentrated on the conversion

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\* References are given at the end of this report.

of decaborane in a stepwise fashion to carborane. The hitherto unreported dialkenyl-carborane, 1,2-bis(3-butenyl)carborane, was prepared by the reaction of dilithio-carborane with 4-bromo-1-butene. During the second quarter <sup>(3)</sup>, mono(epoxybutyl)-carborane was prepared and its catalyzed polymerization to a polyether was demonstrated. During the current quarter, the program made considerable progress into the preparation and polymerization of bis(epoxybutyl)carborane and an evaluation of its adhesive bond properties.

## II. DISCUSSION

### A. Technical Approach

The project has been divided into the following four phases:

- I. Synthesis of alkenylcarborane and dialkenylcarborane intermediates.
- II. Synthesis of carborane-epoxy monomers.
- III. Curing and polymerization studies.
- IV. Adhesive bond property evaluation.

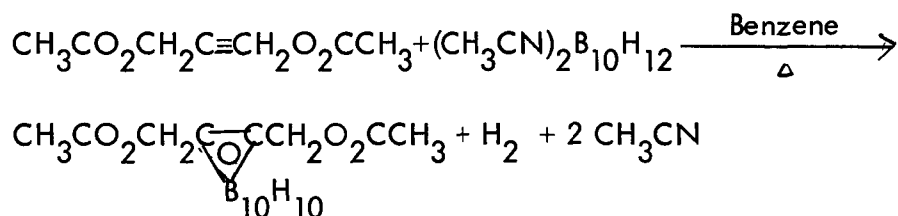
The major effort during the present quarter was devoted mainly to Phase I, II, and III. An evaluation of adhesive bond properties (Phase IV) was initiated.

### B. Technical Progress

#### 1. Phase I - Synthesis of Intermediates

##### a. 1,2-Bis(acetoxymethyl)carborane (BAMC)

The preparation of 1,2-bis(acetoxymethyl)carborane was carried out according to the following equation:

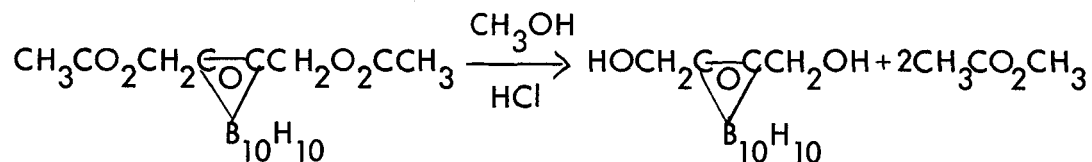


Five 175 gm batches (Numbers 7-11) of 6,9-bis(acetonitrilo)decaborane (BAND) were converted to BAMC. A total of 555 gm. of BAMC was obtained for an over-all conversion of reactant BAND to product of 44 percent.



b. 1,2-Bis(hydroxymethyl)carborane (BHMC)

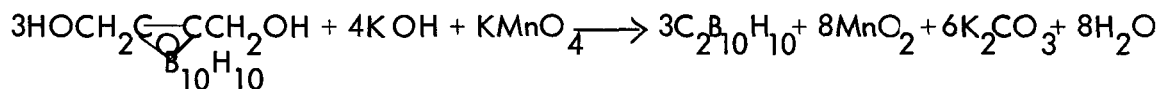
The carborane diol was prepared by the acid-catalyzed transesterification of BAMC.



A total of 550 gm. of BAMC was treated in the above manner (Batch Number 3). Recrystallization from water in seven batches gave 162 gm. of pure white material. Data collected on two of these batches showed that as much as 19% of the crude product was retained in the water solvent. This apparent loss might be due to the solubility of BHMC or of an impurity. The over-all conversion of reactant BAMC to product was 42 percent.

c. Carborane

The preparation of carborane was carried out according to the following equation.



A total of 71.5 gm. of carborane was obtained from four batches (Numbers 10 - 13) utilizing 40.6 gm. portions of BHMC. The amount of carborane obtained represented an over-all conversion of 62% of BHMC to desired product.

d. 1,2-Bis(3-butenyl)carborane

A reaction to form 1,2-bis(3-butenyl)carborane was summarized in the Second Quarterly Progress Report. This reaction utilized butyllithium in hexane solution as obtained from Foote Chemical Company. The reaction

was repeated to give the following fractions:

<u>Fraction</u>	<u>Amount (gm)</u>	<u>M.P. °C</u>
I	3.3	71-73
II	4.6	71-73
III	2.4	70-72
IV	0.6	62-68

The infrared spectra of all four fractions were essentially identical and were similar to the spectrum of a product (m.p. of 70-72°C) isolated from a previous preparation and characterized by elemental analysis. Fractions I, II, and III can be combined and treated as dibutenyl-carborane.

e. 1,2-Bis(5-hexenyl)carborane

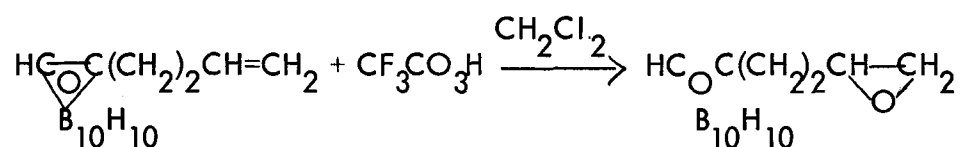
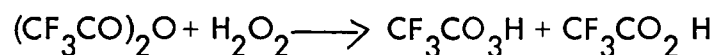
In the previously reported reaction, very little of the dilithiocarborane intermediate appeared to react with 6-bromo-1-hexene. Work-up of the reaction mixture showed that considerable organolithium activity remained in solution. The preparation was therefore repeated, but the reflux period was extended to about ten hours. Complete reaction appeared to have occurred, and a yellow oil was isolated upon removal of ether solvent. The infrared spectrum of the product was compared to the spectra of carborane and 6-bromo-1-hexene. The only significant feature to be expected in the spectrum of the product would be the lack of carborane C-H stretch at  $3075\text{ cm}^{-1}$ . However, the bromohexene also absorbs in this region ( $3080\text{ cm}^{-1}$ ). Spectral analysis of the product was therefore made by a ratio method. The product appears to be of high purity since the ratio of the C-H stretch at  $3080\text{ cm}^{-1}$  to the C=C absorption at  $1640\text{ cm}^{-1}$  is identical to that in 6-bromo-1-hexene. A

total of 26.8 gram of product was isolated representing an 87% conversion of carborane. Elemental analysis of the distilled material should confirm the formation of the desired product.

## 2. Phase II - Synthesis of Epoxy Monomers

### a. Mono(epoxybutyl)carborane

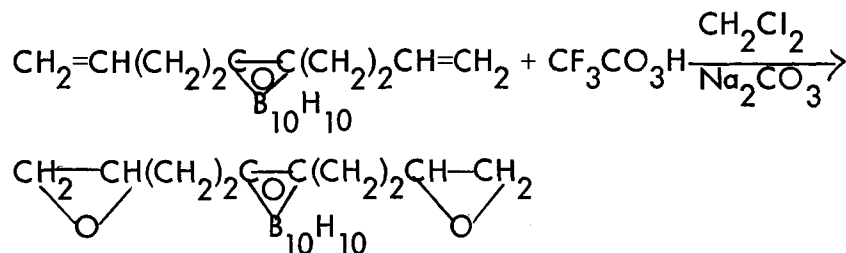
The preparation of epoxybutylcarborane as described in the Second Quarterly Progress Report was repeated except that the amounts of reagents were doubled.



No difficulty was encountered using the larger amounts of 90% hydrogen peroxide. However, the product isolated (7.9 gm) had a melting point of 51–60°C as compared to the previous value of 60–62°C. This range, as well as an examination of the infrared spectrum, showed that incomplete reaction had occurred. Further scale-up work will probably require a longer reaction period or an excess of trifluoroperacetic acid.

### b. Bis(epoxybutyl)carborane

In an initial reaction, dibutenylcarborane was reacted with trifluoroperacetic acid using the standard epoxidation procedure.

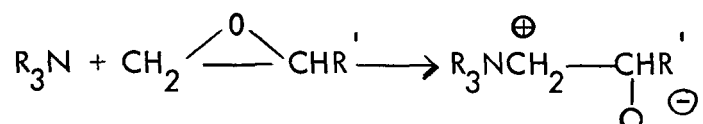


A total of 3.4 gm. of diepoxy product having a melting point of 68-71°C was isolated. The infrared spectrum of the solid contained epoxy bands at 840, 855, and 1410  $\text{cm}^{-1}$ . The ratio of the peak at 910  $\text{cm}^{-1}$  ( $\text{CH}_2$  out of plane deformation of the  $-\text{CH}=\text{CH}_2$  group) to that of the peak at 720  $\text{cm}^{-1}$  (carborane cage vibration) was 1.66. The corresponding ratio in the starting material is 6.5. This comparison shows that the expected epoxy had formed but that unreacted starting material is present. The preparation was repeated a second time using double the amount of epoxidizing agent. The ratio of the above infrared absorption peaks in the product (3.6 gm) decreased to 1.25 indicating that a more complete reaction had taken place. Elemental analyses are pending.

### 3. Phase III Curing Studies

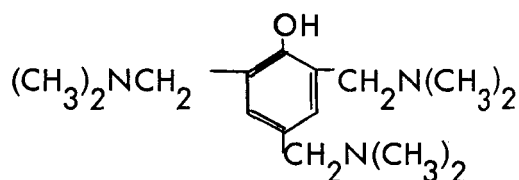
#### a. Background

In order to limit the introduction of relatively less thermally stable organic moieties into the cured system in any large amount, a catalytic system was desired over that involving a reactive hardener. Catalytic systems (e.g. tertiary amines) cure in the following fashion:



The negative portion of the molecule proceeds to attack another epoxide linkage etc., resulting in a very long chain system. In this case, the number of molecules needed to initiate polymerization is limited.

An initial examination (Quarterly Report Number Two) <sup>(3)</sup> had previously been made of the polymerization characteristics of mono(epoxybutyl)carborane. The catalyst chosen to initiate the polymerization was DMP-30; tris (dimethylaminomethyl)phenol.



This substance is considered to be one of the more reactive catalysts since it contains three tertiary nitrogen atoms. The melting point of mono(epoxybutyl)carborane of 60-63° C dictated that a higher temperature would have to be used for a homogenous polymerization. Accordingly, one gram samples of the epoxy were heated at 80-90° C. With 20 drops of DMP-30 catalyst, the epoxy turned to a non-flowing viscous liquid in 30 minutes. With 5 drops of catalyst, the same consistency was obtained within a one hour period. Brittle solids were obtained when the samples were cooled to room temperature. The infrared spectra of the products showed that a portion of the epoxy linkages had been destroyed and that a linear polyether structure had formed.



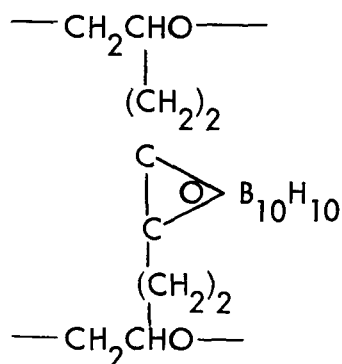
In each case, only a slight increase in solution viscosity was noted at 175°C but viscous plastics having string-forming characteristics formed when the samples were cooled to room temperature. Infrared spectra on all three samples showed broad absorption in the 1060-1150 cm<sup>-1</sup> region. This is characteristic of the ether linkage in cured epoxies. The infrared spectra also showed the expected decrease in the epoxy absorption at 855 cm<sup>-1</sup> relative to the carborane cage absorption at 728 cm<sup>-1</sup>.

Control experiments were run under identical conditions using the epoxy itself to rule out a spontaneous thermal curing mechanism. The behavior of butenylcarborane was also studied in the presence of DMP-30 catalyst. The purpose of the latter reaction was to observe if the amine degraded the carborane cage under these conditions. There was no visual or infrared evidence of reaction or degradation in either system.

A one gram sample of the carborane epoxy with the boron trifluoride-ethylamine catalyst was heated at 85-90°C for one hour. Little, if any, polymerization had taken place under these conditions. This is not unexpected since the literature specifies that curing takes place in this catalytic system only at temperatures greater than 90°C. (4)

#### c. Polymerization of Bis(epoxybutyl)carborane

A highly cross-linked polyether structure would be expected to result from curing of this bi-functional epoxy carborane.





Exploratory curing studies on bis(epoxybutyl)carborane were conducted in a manner similar to those described above. With the  $\text{BF}_3:\text{EtNH}_2$  catalyst, a solid formed almost immediately at  $180^\circ\text{C}$  from the initial melt. The solid was hard at room temperature and not easily fractured by impact with a sharp instrument. However, it did not appear homogeneous, probably the result of too rapid a cure.

With N,N-dimethylbenzylamine as catalyst, the bis(epoxybutyl)carborane system remained a free flowing liquid at  $180^\circ\text{C}$ . A solid, that was brittle and easily fractured, formed when the sample cooled to room temperature.

DMP-30 catalyst cured the diepoxy system to a spongy mass which turned to a brittle solid when cooled to room temperature.

Since our initial studies above had indicated that the  $\text{BF}_3:\text{EtNH}_2$  system appeared to be the most promising, an investigation was made of curing at lower temperatures. After curing for 1/2 hour at  $80-90^\circ\text{C}$ , very little change in solution viscosity was noted. An additional two hours of heating gave a viscous liquid at  $90^\circ\text{C}$ , and a viscous plastic formed when the sample was cooled to room temperature. An additional treatment at  $120^\circ\text{C}$  for three hours gave a soft solid at this temperature, but a hard solid, not easily fractured, formed on cooling to room temperature.

A fresh sample was then heated at  $150^\circ\text{C}$ . After 15 minutes, a non-flowing viscous liquid had formed at this temperature. After one hour, the sample was a hard solid at  $150^\circ\text{C}$  which, at room temperature, was not easily fractured. This encouraging result suggested that lap-shear specimens be assembled in this system. The results of this work are described in a following section.

#### d. Polymerization of the Mixed Mono-and Bis(epoxybutyl)carborane System

Equal weight mixtures of the two epoxycarborane materials were treated with the same three curing agents at  $180^\circ\text{C}$ . Under these conditions, curing resulted in brittle solids.

e. Use of Bis(hydroxymethyl)carborane (BHMC) Additive

Mixtures of the two carborane epoxies were cured in the presence of BHMC with both DMP-30 and N,N-dimethylbenzylamine catalyst at 180°C. The purpose of this work was to introduce a flexibilizer into the system that would react by way of its two hydroxyl groups. However, in both cases, materials were obtained which were brittle solids at room temperature.

#### 4. Phase IV--Testing Program

##### a. Initial Lap-Shear Specimens from Mono(epoxybutyl)carborane

In this first series of experiments, we were mainly interested in developing techniques for the lap shear studies to follow. Stainless steel (303) specimens were treated (as per Mil. Spec. MIL-A-005090E, p. 19) utilizing methylethylketone, HF-HNO<sub>3</sub>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>, and water washing. DMP-30 catalyst (18 drops) was added to 3.7 gm of liquid epoxybutylcarborane at about 80°C. The resulting liquid, which contained some bubbles, was applied to the preheated specimens. The specimens were assembled and placed in an air oven at 110° C for 20 hours. The only pressure at the joints was that of the top specimen itself. Little or no cohesion was observed after the samples had cooled to room temperature. The solid that did adhere to the steel surface was brittle and easily removed by scratching. The remainder of the resin, after having stood for several days at room temperature, was reheated to about 80°C. The sticky solid was applied to specimens along with Volan A-181 glass cloth to aid in holding the resin in place. The specimens were assembled in a Carver Press and treated at 175° C and 100 psi for one hour. Again, no cohesion was observed and the assemblies easily separated. However, the cured epoxy did appear to "wet" the metal surface.

##### b. Lap-Shear Specimens Using Bis(epoxybutyl)carborane

Type 17/7 stainless steel specimens were used in the following studies. A number of strips were machined according to Mil Spec MIL-A-00509E. The final strip dimensions were 5.094 in x 1.000 in x 0.050 in. Each lap-shear specimen consisted of two of the above strips overlapped by 0.5 in. Each strip was cleaned and etched in the manner outlined in (a).

Two grams of bis(epoxybutyl)carborane was mixed with < 0.2 gm of BF<sub>3</sub>EtNH<sub>2</sub> curing agent. The mixture was corked in the test tube and heated to 90° C resulting in a milky colored liquid. When this liquid was applied to the stainless steel strips it solidified almost immediately.

Twelve of the stainless steel strips were treated in the above manner. Three specimens were assembled and placed in an air oven at 150° C for 1 hour. No external pressure was applied during this treatment. On cooling to room-temperature there appeared to be a good bond at the interface. The remaining three specimens were assembled in a slightly different manner to that described above. In these specimens, the milky liquid was applied to the surface together with Volan A-181 glass cloth which aided in holding the resin in place. They were then assembled in a Carver Press and heated at 150° C and 130 p.s.i. for 1 hour. On cooling to room temperature, there again appeared to be a good bond at the interface.

#### c. Instron Tests

All six of the specimens were tested in an Instron tensile machine at a constant strain rate of 0.01 in/in/min. This strain rate gave a test time which ranged between 1.9 mins. and 2.4 minutes. The three specimens prepared without any external pressure had bond strengths of 1460 p.s.i., 1560 p.s.i., and 1290 p.s.i. In the latter case, the bond was observed to be wedge-shaped which would account for the low value of the breaking stress observed. After failure, the surfaces were examined to determine the mode of failure. Two of the specimens (1460 p.s.i. and 1290 p.s.i.) exhibited adhesive failure. Failure of the third (and strongest) specimen was difficult to characterize. It appeared to be a mixture of cohesive and adhesive failure. The lap shear specimens prepared with the glass cloth and under pressure, showed a much larger scatter in the results. Bond strengths of 1560 p.s.i., 1200 p.s.i., and 1090 p.s.i. were measured in these specimens. Because of the glass cloth in the joints, it was more difficult to establish the mode of failure in these cases. However, they did appear to be cohesive rather than adhesive.

#### d. Evaluation of Results

The applicability of polymerized epoxyalkylcarborane systems as adhesives has now been demonstrated. Bis(epoxybutyl)carborane, cured at 150° C with the boron trifluoride: monoethylamine catalyst, can be used to construct lap-shear specimens using 17/7 stainless steel. Although the results of the tensile tests on the first samples are far from spectacular, a thorough investigation of the curing system as well as an improvement in lay-up condition should substantially improve the magnitude of the specimen tensile strength.

Failure to obtain satisfactory results in the preliminary tests on fabrication of lap-shear specimens in the amine system is probably due to the absence of cross-linking since only the monofunctional(epoxybutyl)carborane was used. This result was not unexpected since studies on bulk systems showed that this epoxy cured to a brittle solid. Since the same result was obtained on bulk samples of the bis(epoxybutyl)carborane, no attempt was made to assemble lap-shear specimens in that system. Here again, the formation of brittle solids, unsatisfactory for adhesive studies, might be due to a lack of cross-linking. Alternatively, too extensive cross-linking might have taken place to freeze the molecules into position and restrict their freedom of motion.

It should be noted that to date, the samples of epoxybutylcarborane which have been used for testing were probable impure. Possible impurities are unreacted carborane, and unreacted alkenylcarborane. These impurities will not enter into the curing reaction but will act as an additive. Thus, they might have some overall effect on the physical properties of the resulting cured epoxy.

### III. FUTURE WORK

Efforts during the fourth quarter will concentrate on Phase IV, adhesive bond property evaluation. In addition, work will be continued on Phases I and II, synthesis of the required epoxy compounds, and Phase III, curing and polymerization studies.

The testing program will be continued on the bis(epoxybutyl)carborane-boron trifluoride ethylamine system.

Pending the availability of significant quantities of the epoxycarborane and bis(epoxyalkyl)-carborane monomers, the adhesive testing program will also be directed toward a study of commercially available adhesives which have similar curing and relatively good elevated temperature properties. Two Shell Epon adhesives have been selected on the basis of these considerations. Both Epon 929 and 934 have curing temperatures in the 300° F range and have tensile shear strengths of 3-4000 psi at 400° F, falling off to approximately 500 psi at 500° F.

Two new carborane based polymers, synthesized on a separate program, will also be tested for comparative data. One compound is a urethane polymer prepared from bis(hydroxymethyl)-carborane and methylenebis (p-phenyl)isocyanate. The second is a dimethylsiloxane formulation incorporating bis(hydroxymethyl)carborane and silicon phthalocyanine. The adherence of both materials to steel and to glass substrates suggests that they may have good adhesive properties. In addition, these new polymers are thermally stable and appear to be quite tough.

Supplies of mono- and bis(epoxyalkyl)carborane and the alkenylcarborane precursors will be replenished for curing studies and the testing program.

Curing studies on bulk samples will be continued to determine which system would show the most promise in the testing program.

In order to prepare the test specimens, a constant pressure of 100 psi is required on the epoxy joint during the curing process. After consultation with the design engineers of Fred S. Carver Inc., Hydraulic Equipment, a standard hydraulic press together with a specially modified quick closure attachment has been ordered. The latter, which will be operated by cylinder nitrogen, will enable constant pressures up to 300 pounds to be maintained for periods up to two hours.

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